

73N18965

NASA TECHNICAL NOTE



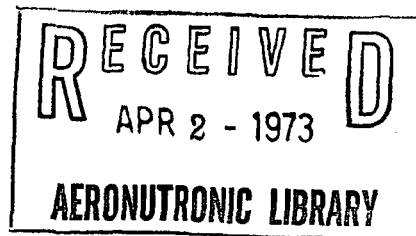
NASA TN D-7113

NASA TN D-7113

**MEASURED CATALYCITIES OF
VARIOUS CANDIDATE SPACE SHUTTLE
THERMAL PROTECTION SYSTEM
COATINGS AT LOW TEMPERATURES**

by Carl D. Scott

*Manned Spacecraft Center
Houston, Texas 77058*



1. Report No. NASA TN D-7113	2. Government Accession No.	3. Recipient's Catalog No.	
4. Title and Subtitle MEASURED CATALYCITIES OF VARIOUS CANDIDATE SPACE SHUTTLE THERMAL PROTECTION SYSTEM COATINGS AT LOW TEMPERATURES		5. Report Date March 1973	
		6. Performing Organization Code	
7. Author(s) Carl D. Scott, MSC		8. Performing Organization Report No. MSC S-348	
9. Performing Organization Name and Address Manned Spacecraft Center Houston, Texas 77058		10. Work Unit No. 908-42-02-00-72	
		11. Contract or Grant No.	
12. Sponsoring Agency Name and Address National Aeronautics and Space Administration Washington, D.C. 20546		13. Type of Report and Period Covered Technical Note	
		14. Sponsoring Agency Code	
15. Supplementary Notes			
16. Abstract <p>Atom-recombination catalytic rates for surface coatings of various candidate thermal protection system materials for the space shuttle vehicle were obtained from measurements in arc-jet air flow. The coatings, chrome oxides, siliconized carbon/carbon, hafnium/tantalum carbide on carbon/carbon, and niobium silicide, were bonded to the sensitive surface of transient-slug calorimeters that measured the heat-transfer rates to the coatings. The catalytic rates were inferred from these heat-transfer rates. Surface temperatures of the calorimeters varied from approximately 300° to 410° K.</p> <p>The heating rates, relative to a fully catalytic surface, were calculated using a specified formula. The chemical composition and other flow properties necessary for the calculation were computed by use of a nonequilibrium nozzle-flow computer program. Comparison of the heating rates measured on nickel-coated reference calorimeters with these calculations agreed to within 6 percent. Based on this reference, catalycities for the other materials were inferred by comparing measured and calculated heating rates. The chrome oxides and oxidation-inhibited carbon/carbon had the lowest catalytic rates in the temperature range of these measurements. This low catalycity enhances the desirability of these surfaces as a space shuttle thermal protection system coating.</p>			
17. Key Words (Suggested by Author(s)) <ul style="list-style-type: none"> * Catalysis * Thermal Protection * Space Shuttle * Heat Transfer * Calorimeter 		18. Distribution Statement	
19. Security Classif. (of this report) None	20. Security Classif. (of this page) None	21. No. of Pages 23	22. Price \$3.00

MEASURED CATALYCITIES OF VARIOUS CANDIDATE SPACE
SHUTTLE THERMAL PROTECTION SYSTEM COATINGS AT
LOW TEMPERATURES

By Carl D. Scott
Manned Spacecraft Center

SUMMARY

The atom-recombination catalytic rates for surface coatings of various candidate thermal protection system materials for the space shuttle vehicle were obtained from measurements in arc-jet flows of air at two enthalpy levels (approximately 15 and 46 MJ/kg). These catalytic rates were compared with measurements on selected materials having both low and high catalycities (for example, Teflon, gold, platinum, nickel, and copper). The candidate space shuttle material coatings were chrome oxides in borosilicate glass, siliconized carbon/carbon, hafnium/tantalum carbide on carbon/carbon, and niobium (formerly known as columbium) silicide. These materials were bonded to the sensitive surface of transient-slug calorimeters to measure the heat-transfer rates to the coatings from which the recombination rates were deduced. The calorimeters were installed in a two-dimensional rectangular model that was inserted into the flow from the arc-jet. Surface temperatures of the calorimeters varied from approximately 300° to 410° K.

The heating rates, relative to a fully catalytic surface, were calculated using a formula given by Ronald B. Pope and R. Goulard. The chemical composition and other flow properties necessary for the calculation were computed by the use of a nonequilibrium nozzle-flow computer program. A comparison of the heating rates measured on nickel-coated reference calorimeters with these calculations agrees to within 6 percent. Based on this reference, catalycities for the other materials were inferred by comparing measured and calculated heating rates. Certain of the materials tested had low catalytic rates in the temperature range of these measurements. This low catalycity enhances the desirability of these surfaces as a space shuttle thermal protection system coating.

INTRODUCTION

In this report on catalycities,¹ measurements of the catalytic recombination of air atoms on a number of candidate space shuttle/orbiter thermal protection system (TPS) materials are described. Because the space shuttle will be a multiflight vehicle, the materials must be reusable for many flights. The design and evaluation of a TPS for many cycles requires far greater precision than for a single-flight system. The performance of these materials in the flight environment must be predicted accurately. This prediction requires a thorough understanding of the flight environment, the ground-test environments, and the interaction of these environments with the materials. In particular, the heating rate depends on the catalytic efficiency of the material surface.

Catalycity is an important factor to be considered in predicting heating rates to the space shuttle vehicle and to models tested in ground facilities. It is particularly important in arc-tunnel facilities in which there is a significant amount of free-stream dissociation because of the low density in the nozzle. At these low densities, the recombination rates are slow, and the free-stream dissociation can, therefore, provide a significant potential for catalytic effects at the surface.

The effect of surface catalytic recombination on the aerothermodynamic heating of materials when subjected to high-enthalpy dissociated flows has been considered theoretically by a number of investigators (refs. 1 to 6). These authors (among others) have shown that a significant potential for heating-rate reduction exists if the material has a low recombination catalycity. The reduction in heating rate depends on the degree of dissociation of the gas and on the atom-recombination rate on the material surface. This recombination is governed by the surface catalytic rate. Recombination on the surface liberates the energy of dissociation to the surface. Therefore, if recombination is inhibited by a noncatalytic surface, the heating rate will be less than that experienced by a catalytic surface. The degree of dissociation in the gas depends on a total enthalpy and other flow-field parameters. Because these parameters differ in flight and ground tests, knowledge of the surface catalytic recombination rate is necessary to calculate the heating rate to the material surface for each case. In addition, to predict the heating rates accurately, it is necessary to include coupling of the nonequilibrium viscous-flow field with the effects of the material on the flow properties.

Goulard (ref. 2) showed that the stagnation-point heating rate on a noncatalytic surface could be as low as one-third of the fully catalytic heating rate in the stagnation region of a body having an effective radius of 100 centimeters at conditions comparable to those at shuttle-orbiter peak heating. Equilibrium inviscid flow behind the normal shock and an essentially frozen boundary layer were assumed in that study. Chung (ref. 3) did a simplified nonequilibrium chemistry calculation that included a viscous shock-layer. His results showed that the heating rate to a noncatalytic wall is as low as one-third of the equilibrium heating rate in the stagnation region of bodies having effective radii of 30 and 150 centimeters at altitudes of 73.5 and 84.0 kilometers,

¹Catalycity is used in this report to denote the tendency of a surface to promote chemical reactions on the surface without itself undergoing a chemical reaction. The term is also used synonymously with catalytic rate.

respectively. Inger (ref. 4) did a similar calculation but allowed for effects of shock slip. His results agreed with those of Chung. Both neglected variation of transport properties behind the shock. Tong and Suzuki (ref. 5) calculated the stagnation-point heating-rate reduction assuming viscous-shock-layer equations with a binary-air-chemistry model and constant-transport properties. Their heating-rate reduction for a noncatalytic surface was consistent with the previous investigations. Chung, Holt, and Liu (ref. 6) formulated a numerical solution to the Navier-Stokes equations in the stagnation region of a blunt body. Their calculations were for a fluid flow in the viscous merged-layer regime with nonequilibrium chemical reactions and included species diffusion. These conditions are typical of shuttle entry at an altitude of approximately 90 kilometers, which is where peak heating begins. The results showed that the ratio of the heating rate for a noncatalytic surface to that of a fully catalytic surface is approximately one-half.

A number of experiments have been performed that show reduction in heating rates because of noncatalytic materials. For example, Hartunian and Thompson (ref. 7) made differential heating-rate measurements in a shock tube on a hemisphere having a radius of 2.54 centimeters. Mixtures of oxygen and argon were used as the test gas to study only the effects of oxygen dissociation. The measured ratio of the heating rate on silicon oxide to the heating rate on silver at a shock Mach number of 6 and a free-stream static pressure of 200 N/m^2 (1.5 torr) was 0.82. At these test conditions, the enthalpy (and, therefore, potentially the dissociation) is lower than that at typical-flight peak-heating conditions for the shuttle. Pope (ref. 8) measured heating rates on the order of one-third of the fully catalytic value for low catalycity materials. This value corresponds to the maximum shuttle-entry enthalpy after taking pressure and model diameter into account. These measurements were made in an arc-heated wind tunnel. Pope correlated his results with a theoretical formula of Goulard (ref. 2) to obtain the surface catalytic rate k_w for several materials.

The effect of catalycity on heat transfer away from the stagnation point has not been investigated sufficiently to assess its importance to the space shuttle. Such an investigation would involve detailed flow-field calculations that are beyond the scope of this work. Because surface catalycity is an important parameter in predicting the heating rate and in interpreting heating-rate measurements, knowledge of the catalytic rate k_w is needed for materials used in heat-transfer measurements and for materials that are proposed for testing and flight. The experimental and analytical techniques used to determine the catalycity for several candidate space shuttle vehicle coatings are described further.

The author expresses his gratitude to Charles Allton of the NASA Manned Spacecraft Center (MSC) for his supervision of the model and sensor design and fabrication.

SYMBOLS

c_p specific heat at constant pressure

D diffusion coefficient

h	altitude
h_D°	enthalpy of formation of atoms
h_t	total enthalpy
H_e	total enthalpy at edge of boundary layer
k_w	catalytic rate constant
Le	Lewis number, $Le = \frac{\rho D c_p}{\lambda}$
M	molecular weight
Pr	Prandtl number, $Pr = \frac{\mu c_p}{\lambda}$
P_s	stagnation point pressure
q	heat-transfer rate
q_{FC}	heat-transfer rate to a fully catalytic surface
q_{ref}	heat-transfer rate to a reference coating
R	effective nose radius
\bar{R}	universal gas constant
Re	Reynolds number $= \frac{\mu_\infty \rho_\infty R}{\mu_\infty}$
Sc	Schmidt number $= \frac{\mu}{\rho D} = \frac{Pr}{Le}$
T	temperature
u	velocity
α_e	mass fraction of molecules dissociated at edge of boundary layer
γ	ratio of specific heats

γ_w	catalytic efficiency of surface
$\bar{\gamma}_w$	average catalytic efficiency of surface
λ	thermal conductivity
μ	dynamic viscosity
ρ	density
ϕ	a quantity defined by equation (2)

Subscripts:

e	edge of boundary layer
FC	fully catalytic
s	stagnation point
t	total
w	wall
∞	free stream

EXPERIMENTS

Experiments to determine catalycity for the TPS coatings were performed in the MSC 10-megawatt Arc Tunnel Facility using a dual-tandem tube-constricted arc heater with average enthalpies of 15 and 46 MJ/kg. The catalycity measurements were made at the low enthalpy, where only the oxygen is dissociated, and at the high enthalpy, where almost all the nitrogen is dissociated as well. The air flow was expanded through a conical nozzle having a 15° half-angle divergence and a 3.81-centimeter-diameter throat and 50.8-centimeter-diameter exit. This flow was far from chemical equilibrium. A summary of average experimental conditions is given in table I.

The coated-slug calorimeters that were used to make the heating-rate measurements were smaller but of the same basic design as those used in the tests of reference 9. The diameter of the slug was 0.80 centimeter. A sketch of the calorimeter is shown in figure 1. The reference calorimeters were plated with nickel, and the other calorimeters were coated with various materials that are listed in table II and described in the appendix.

Several of the coatings were materials having known surface catalycity: platinum, gold, and Teflon. The other materials were candidate TPS coatings: silicon carbides, hafnium/tantalum carbide, niobium silicide, and chrome oxides.

TABLE I. - SUMMARY OF AVERAGE EXPERIMENTAL CONDITIONS

Property	High enthalpy	Low enthalpy
Nozzle throat diameter, cm	3.81	3.81
Gas-flow rate, g/sec	14.26	41.8
Plenum pressure		
N/m ²	44800	86900
atm442	.858
Total enthalpy, MJ/kg	46.8	15.3
Mach number	9	8
Free-stream molecular weight	14.49	22.01
Pitot pressure		
N/m ²	600	820
atm00592	.0081
$(q\sqrt{R})_{FC}^{FF^a}$, W/m ^{3/2}	1.99×10^6	$.877 \times 10^6$
Reynolds number	94	190
Specific-heat ratio	1.658	1.484

^aCalculated heating rate to a fully catalytic flat-faced cylinder normalized to unit radius.

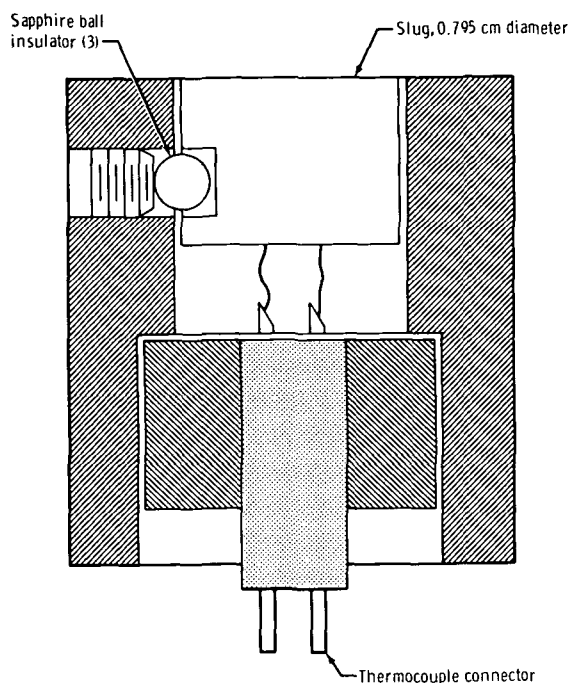


Figure 1. - Diagram of slug calorimeter.

All of the calorimeter slugs were made of oxygen-free copper, except the one used for the niobium-silicide coating; that coating was made of niobium alloy 752. Each coating was applied to two calorimeters for redundancy and for an indication of reproducibility.

The calorimeters were mounted in two rectangular parallelepiped models that accepted six calorimeters each along the stagnation line (fig. 2). One of these models had six nickel-coated calorimeters and was used as the reference for all measurements. The other model contained six calorimeters that had different coatings. These models were inserted alternately into the flow for a few seconds until the thermocouple on the slug reached a maximum temperature of 400° to 450° K. The insertion speed was such that the transient-heating-rate effects could be neglected.

TABLE II. - CALORIMETER COATINGS

Coating	Thickness, cm
Nickel	0.0013
Gold	.0013
Platinum	.0013
Teflon	.0013
Siliconized carbon/carbon	.038 to .090
Hafnium/tantalum carbide on carbon/carbon	.038 to .048
Niobium silicide	--
Chrome oxide 1	.020 to .018
Chrome oxide 2	--
Silicon carbide/silicon	--

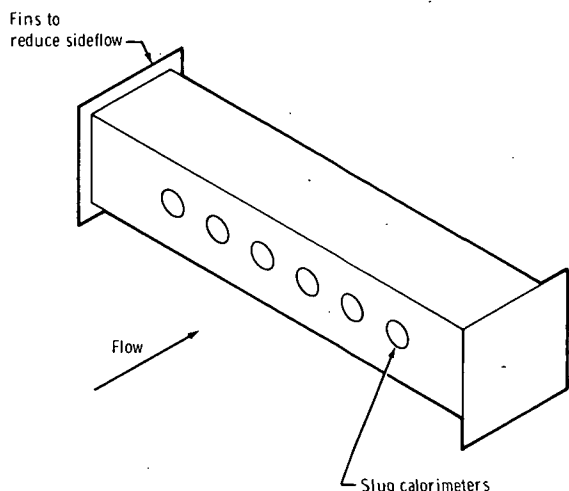


Figure 2. - Diagram of slug-calorimeter holder.

Pilot pressures were measured with a 1.27-centimeter-diameter flat-faced probe. The probe, when swept through the flow to determine uniformity, indicated pressure variations of approximately 15 percent over the width of the test model. However, because each coating was compared with a reference sensor at the same location with respect to the flow, these small variations in the flow field were not considered significant.

Precautions were taken to ensure that the surface coatings were not contaminated with foreign matter (such as oils). However, adsorbed gas molecules or oxides were not removed; thus, the coatings were kept in a normal test or flight condition.

THEORY AND ANALYSIS

The catalytic rates k_w of the various coatings were inferred by comparing the ratio of the measured heating rates to fully catalytic heating rates predicted by the use of a nonequilibrium nozzle-flow computer program with the ratio q/q_{FC} predicted by Goulard's formula (ref. 2) as given by Pope (ref. 8).

The nozzle-flow computer program is based on one-dimensional nonequilibrium analysis (ref. 10) as modified and expanded by W. L. Bade under a NASA contract. This program is used to compute reservoir conditions based on plenum pressure and mass-flow rate or total temperature. Free-stream properties, such as temperature, static pressure, density, velocity, Mach number, and species concentrations, are calculated at stations down the nozzle. At specified locations in the nozzle, the program calculates conditions behind a normal shock by iterating on a set of Rankine-Hugoniot relations. The composition behind the shock is assumed to be frozen at the free-stream composition. This assumption is considered valid because it is based on the calculations of Gibson and Marrone (refs. 11 and 12), which show that the shock-standoff distance in a Lighthill gas is much less than the recombination-zone thickness for the present conditions.

In the nozzle-flow computer program, the fully catalytic heating rate to a flat-faced cylinder is calculated by using the correlation formula of Fay and Riddell (ref. 1), and the velocity-gradient parameter is obtained from a curve fit of the results of Vinokur (ref. 13) for the stagnation point of a flat-faced cylinder. The measured heating rates to a flat-faced bar (two-dimensional geometry) are converted to an equivalent

heating rate to a flat-faced cylinder (axisymmetric geometry) by multiplying the measured values by $\sqrt{2}$ or, equivalently, by multiplying the effective diameter by 2. This procedure is analogous to the relation between the Newtonian velocity gradient on a hemisphere compared with that of an infinite circular cylinder.

Other properties behind the normal shock at the stagnation point are evaluated by use of the program. Among these properties are the temperature T_s , pressure P_s , density ρ_s , viscosity μ_e , Prandtl number Pr , and Lewis number Le .

The ratio q/q_{FC} of the heating rate to a surface having a catalycity k_w to that of a fully catalytic surface is that of Goulard's (ref. 2) as given by Pope (ref. 8).

$$\frac{q}{q_{FC}} = 1 - \frac{Le^{2/3} \frac{(\alpha_e h_D^\circ)}{H_e}}{1 + (Le^{2/3} - 1) \frac{(\alpha_e h_D^\circ)}{H_e}} (1 - \phi) \quad (1)$$

where H_e is the total enthalpy at the edge of the boundary layer (assumed to be equal to total stagnation enthalpy h_t) and $\alpha_e h_D^\circ$ is the total energy available for release in surface reactions. In a simplified single element gas, α_e is the atom fraction and h_D° is the dissociation energy per unit mass.

The term ϕ is defined as

$$\phi = \left\{ 1 + \frac{0.665 T_w}{Sc^{2/3} k_w} \left(\frac{\bar{R} \mu_e}{R P_s T_e M} \right)^{1/2} u_\infty \left[\frac{\rho_\infty}{\rho_e} \left(2 - \frac{\rho_\infty}{\rho_e} \right) \right]^{1/4} \right\}^{-1} \quad (2)$$

where T_w is the wall temperature; \bar{R} is the universal gas constant; M is the molecular weight; P_s is the stagnation point pressure; R is the effective model radius; T_e is the temperature; u_∞ is the free-stream velocity; ρ_∞ and ρ_e are the densities in the free stream and in the shock layer, respectively, and $Sc = Pr/Le$ is the Schmidt number. The values of these parameters for the frozen gas mixture were obtained from the nozzle-flow computer program. By using these values in equations (1) and (2), the ratio q/q_{FC} was calculated as a function of k_w .

In these equations, quantities pertaining to mixtures are used. The catalyticity k_w also is assumed to apply for the mixture. A more precise calculation would be as given by D. E. Rosner in reference 14, wherein each specie that reacts on the surface is accounted for separately; therefore, the second term in equation (1) becomes a sum over these species. Because this would require knowledge of k_w for oxygen and nitrogen separately and very precise measurements of q , the present method was selected.

Goulard assumed a frozen boundary layer in his analysis. For the experimental conditions used in the present measurements, this is a good assumption because of the low Reynolds number ($Re < 200$). Inger (ref. 4) shows that the boundary layer departs from equilibrium at Reynolds numbers less than 4000; therefore, the boundary layer should be essentially frozen with respect to recombination at $Re < 200$.

Several sensors had relatively thick coatings (approximately 0.05 centimeter) with relatively low thermal conductivities (about one-tenth that of copper). A transient one-dimensional numerical solution of the associated heat transfer and capacitance was performed. This solution was indicative that the effects of the coating on the response of the calorimeter were negligible.

To calculate q/q_{FC} for typical flight conditions, the results of Inger (ref. 4) were used. Inger calculated the relative heating rate q/q_{FC} to a surface as functions of altitude h and catalytic efficiency γ_w . The calculations solved the merged-layer stagnation-point nonequilibrium-flow problem on a sphere based on the assumption of constant Lewis and Prandtl numbers.

RESULTS

Nickel-coated slug calorimeters were used as the reference because nickel forms a durable nonreacting surface and because the catalytic rate of nickel is known. The average heating rates measured on the six nickel-coated reference calorimeters were compared with calculated heating rates for each run condition. Measured arc-heater stagnation pressure and mass-flow rates were used in the nozzle-flow computer program to calculate the total enthalpy. The program then performed a nozzle-expansion calculation and predicted conditions behind a normal shock on a flat-faced infinite cylinder, including the fully catalytic heating rate. This heating rate was multiplied by q_{ref}/q_{FC} obtained from equations (1) and (2). The nickel catalytic rate constant $k_w = 300$ cm/sec given by Pope was used to calculate this ratio. The agreement between the measured and calculated heating rates was within 6 percent. At the high-enthalpy condition, the measured heating rate was 6.05×10^5 W/m² compared with the calculated value of 6.40×10^5 W/m². At the low-enthalpy condition, the measured and calculated heating rates were 3.09×10^5 W/m² and 3.22×10^5 W/m², respectively.

TABLE III. - COMPARISON OF MEASURED AND CALCULATED q/q_{FC} FOR SEVERAL STANDARD COATINGS
 [Calculated values based on Pope's data; $k_w = 300$ cm/sec for nickel]

Coating	$h_t = 46.8$ MJ/kg		$h_t = 15.3$ MJ/kg		k_w^c , cm/sec
	q/q_{FC} measured ^a	q/q_{FC} calculated ^b	q/q_{FC} measured ^a	q/q_{FC} calculated ^b	
Gold	$0.57 \pm .06$	$0.53 \pm .05$	$0.64 \pm .06$	$0.64 \pm .05$	260
Copper	$.62 \pm .06$	$.57 \pm .08$	$.64 \pm .06$	$.68 \pm .07$	380
Teflon	$.47 \pm .05$	$.42 \pm .03$	$.59 \pm .06$	$.53 \pm .03$	<10

^aThis uncertainty stems primarily from the uncertainty in q_{ref}/q_{FC} caused by uncertainty in k_w of nickel and h_t .

^bThis uncertainty stems from the uncertainty in k_w and h_t .

^cThese values of k_w were obtained from reference 8.

TABLE IV. - MEASURED q/q_{FC} AND NET CATALYTIC RATES INFERRED
FROM THESE MEASUREMENTS FOR VARIOUS SHUTTLE THERMAL
PROTECTION SYSTEM COATINGS

Coating	$h_t = 46 \text{ MJ/kg } \begin{smallmatrix} +6 \\ -5 \end{smallmatrix} \text{ percent}$ (a)		$h_t = 15.3 \text{ MJ/kg } \begin{smallmatrix} +16 \\ -7 \end{smallmatrix} \text{ percent}$ (a)	
	$\frac{q}{q_{FC}}$	$k_w, \text{ cm/sec}$	$\frac{q}{q_{FC}}$	$k_w, \text{ cm/sec}$
Chrome oxide 1	0.51	190 $\begin{smallmatrix} +510^a \\ -190 \end{smallmatrix}$	0.57	66 $\begin{smallmatrix} +260^a \\ -66 \end{smallmatrix}$
Chrome oxide 2	.52	230 $\begin{smallmatrix} +130 \\ -134 \end{smallmatrix}$.57	66 $\begin{smallmatrix} +120 \\ -66 \end{smallmatrix}$
Silicon carbide/silicon	.58	400 $\begin{smallmatrix} +140 \\ -130 \end{smallmatrix}$.67	345 $\begin{smallmatrix} +200 \\ -140 \end{smallmatrix}$
Siliconized carbon/carbon	.55	300 $\begin{smallmatrix} +170 \\ -140 \end{smallmatrix}$.62	195 $\begin{smallmatrix} +140 \\ -100 \end{smallmatrix}$
Hafnium/tantalum carbide on carbon/carbon	.54	285 $\begin{smallmatrix} +225 \\ -191 \end{smallmatrix}$.59	115 $\begin{smallmatrix} +180 \\ -115 \end{smallmatrix}$
Niobium silicide	.69	940 $\begin{smallmatrix} +560 \\ -430 \end{smallmatrix}$.79	1200 $\begin{smallmatrix} +200 \\ -320 \end{smallmatrix}$

^aError limits result from the variation in q/q_{FC} because of the maximum variation in total enthalpy for each nominal condition and the statistical uncertainty in the measurements.

To determine the experimental q/q_{FC} for the other materials having a known catalytic constant k_w , the equation

$$\frac{q}{q_{FC}} = \left(\frac{q}{q_{ref}} \right)_{meas} \times \left(\frac{q_{ref}}{q_{FC}} \right)_{calc} \quad (3)$$

was used. The expression q_{ref}/q_{FC} was obtained by using equations (1) and (2). The values of q_{ref}/q_{FC} for the high and low enthalpies were 0.545 and 0.655, respectively. In table III, experimental q/q_{FC} values are compared with those calculated from equations (1) and (2) by using Pope's (ref. 8) values of k_w for several materials of known catalycity. The agreement at both the high- and low-enthalpy conditions is good. There is less than the 10-percent uncertainty in q/q_{FC} because of the uncertainty in k_w . These measured data represent averages of several measurements at each condition. The standard deviation of these measurements caused by random errors is less than 10 percent, and the standard error is less than 5 percent.

Measurements also were made of the relative heating rates to various candidate space-shuttle-vehicle TPS coatings. These ratios were adjusted by the calculated q_{ref}/q_{FC} for the appropriate test condition. The catalytic rates k_w for the candidate coatings were inferred from these ratios of heating rates. The results of these measurements and calculations are shown in table IV. The siliconized carbon/carbon and hafnium/tantalum carbide on carbon/carbon and the silicon carbide/silicon have a k_w that is higher than the chrome oxides but that is low enough to affect the heating rate in arc-heated flows and certain flight regimes.¹ A catalytic rate as high as that measured on niobium silicide is almost fully catalytic with respect to arc-heated flows and flight.

The reason for the differences in the catalytic-rate constants k_w measured at the two enthalpy conditions is not known; however, the reason may be related to the difference between the free-stream chemical composition at the two conditions. The remaining difference is probably the result of experimental errors in the heating-rate measurements and in the accuracy of the true flow properties.

¹The factors in equation (2), such as T_w , P_s , Sc , u_∞ , and μ_e , effectively scale k_w . Physically, the atom surface recombination rate, and hence that part of the heat transfer caused by surface recombination, is governed by the surface-reaction rate and the atom-diffusion rate. If surface recombination is diffusion limited, then k_w is effectively infinite. In most arc-jet flows, surface recombination is not diffusion limited, whereas the separated-flow regions on the leeward side of the space shuttle will be diffusion limited.

The error limits on k_w , shown in table IV, resulted from the variation in q/q_{FC} because of the maximum variation in total enthalpy for each nominal condition and the statistical uncertainty in the measurements. One possible source of a systematic error is contamination of the coatings by contaminants in the arc-heated gas. Although the erosion rate of the arc-heater electrodes is very small, a small amount of copper or copper oxide may be deposited on the calorimeter surfaces after many exposures to the arc-heated flow. The surfaces of the reference sensors discolored very slightly during the course of the experiments, and there was a small increase in the heating rates measured on these sensors compared with the nickel-coated sensors, which were not used repeatedly for reference. This small variation (less than 15 percent) was taken into account in the data reduction.

From the catalytic-rate measurements described above, the catalytic efficiency γ_w can be calculated approximately for small values of γ_w .

$$\gamma_w = k_w \sqrt{\frac{M\pi}{\bar{R}T_w}} \quad (4)$$

Using the catalytic efficiency and Inger's (ref. 4) results, estimates of the reduction in heating rates in flight were obtained for the materials studied here. The catalytic efficiency and heating-rate reduction are shown in table V. The symbol $\bar{\gamma}_w$ is an average based on the high- and low-enthalpy measurements. A significant reduction in the heating rate occurs at the stagnation region and locations on the vehicle where the boundary-layer gas has been processed by the normal shock.

To determine the reduced heating rate attributable to catalytic effects in regions other than the stagnation region on the space-shuttle orbiter, the nonequilibrium viscous-flow-field problem around the space shuttle must be solved. Nonequilibrium chemistry effects are important at altitudes greater than approximately 60 kilometers. The peak heating portion of the space shuttle entry trajectory also occurs at altitudes greater than 60 kilometers. Therefore, nonequilibrium effects should be taken into account when predicting heating rates on the shuttle noncatalytic surfaces.

TABLE V.- EFFECT OF FINITE CATALYCITY OF COATINGS AT A REPRESENTATIVE FLIGHT CONDITION BASED ON MEASUREMENTS OF k_w AND INGER'S NONEQUILIBRIUM STAGNATION-POINT CALCULATIONS FOR A SPHERE

$$[u_\infty = 7.93 \text{ km/sec, } h = 73.1 \text{ km, } R = 0.30 \text{ m, and } T_w = 1500^\circ \text{ K}]$$

Coating	$\bar{\gamma}_w$	Stagnation point, q/q_{FC}
Chrome oxide 1	0.0050	0.70
Chrome oxide 2	.0056	.72
Siliconized carbon/carbon	.010	.84
Hafnium/tantalum carbide on carbon/carbon	.0079	.78
Niobium silicide	.045	.88

CONCLUDING REMARKS

The measurements and calculations obtained during this study have resulted in the following observations.

Measurements on the nickel-coated calorimeters agreed within 6 percent of calculated values when surface catalytic recombination was taken into account. This agreement was obtained despite the approximating assumptions that were used in the calculations. Reasonably good agreement between measurements and calculations also was obtained for other surface materials, the catalytic rates of which were measured by other investigators. These materials were gold, Teflon, and copper.

The study was indicative that the chrome oxide coatings had the lowest catalycity of the materials investigated, niobium silicide had the highest catalycity, and the oxidation-inhibited carbon/carbon coatings were between these extremes. If these trends continue at operational temperature, then significant reductions would be anticipated in the heating rate for the chrome oxide and inhibited carbon/carbon coatings in the regions of the vehicle where the gases at the surface flow through a near-normal shock wave. Smaller heating-rate reduction would be expected elsewhere on the vehicle because of lower degrees of dissociation.

High-temperature catalycity measurements should be made on shuttle thermal protection system material coatings to determine inflight heating-rate reductions. The analyses could be improved by taking into account finite-rate chemistry and viscous effects in the entire shock layer. In the analysis, flow field should be coupled to the wall by including multicomponent species catalycity and slip at the wall. This situation would be preferable to the boundary-layer assumption of Goulard.

Manned Spacecraft Center
National Aeronautics and Space Administration
Houston, Texas, November 7, 1972
908-42-02-00-72

APPENDIX

DESCRIPTIONS OF COATINGS AND APPLICATIONS

Nickel, gold, and platinum were each electroplated on copper slugs to a thickness of 0.0013 centimeter. An electrolytic solution containing brighteners was used. Teflon was applied to a copper slug that had been cleaned by light chemical etching. The Teflon, in liquid form, was dispersed in a catalyzed vinyl-wash-primer bonding agent. The liquid was sprayed on, allowed to dry for 10 minutes, then baked at 589° K for 20 minutes.

Siliconized carbon/carbon and hafnium/tantalum carbide on carbon/carbon coatings were fabricated and attached to the calorimeters in the following manner.

1. Preparation of specimens

a. A series of 1.755-centimeter-diameter coating specimens were cut in half and bonded to 0.751-centimeter-diameter hardened steel pins. The coating front-face surfaces were in contact with the end of the steel pins. A Styron adhesive that has been used in diffusion bonding studies was the bonding agent. This adhesive leaves no residual ash when heated to temperatures greater than 700° K.

b. The bonded specimens were ground to approximately 0.730 centimeter diameter and 0.041 centimeter thick using 240-grit silicon carbide metallographic paper and tap water. Preliminary attachment studies revealed that, when coating thickness was ground to less than 0.025 centimeter thick, extensive cracking occurred, caused by shrinkage stresses created during silver brazing.

c. Thickness measurements were obtained at 30× magnification on a binocular bench microscope.

d. The specimens were electroless nickelplated with approximately 0.0025-centimeter-thick coating to promote wettability during silver brazing. The procedures used in nickel plating are listed as follows.

(1) The hardened steel pin surfaces were masked using platers tape that left only the ground back face and outer diameter specimen surfaces exposed to the plating solutions.

(2) Before immersion in the electroless nickel bath, the specimens were sensitized in a stannous chloride solution and rinsed in tap water, then activated in a palladium chloride solution and rinsed in deionized water.

(3) Electroless nickel plating was performed at $344^{\circ} \pm 18^{\circ}$ K in McDermid J67; then, the pins were rinsed.

e. After rinsing, the steel pins were unmasked and the bonding adhesive was dissolved in toluene. The steel pins were removed, and the specimens were permitted to remain in toluene for 1 additional hour to dissolve the remaining Styron adhesive.

f. The specimens were examined to determine plating adhesion and coating front-face condition before silver brazing to the copper calorimeters.

2. Silver braze attachment of coatings

a. A preliminary brazing investigation was conducted using QQ-S-561 Class 0 at 1172° K and QQ-S-561 Class 4 (Sil-Bond #50) at 950° K with MIL-F-4483-AWS Type 3 (Airco-Sil #12) flux in flowing argon. The higher temperature brazing alloy diffused into the copper and dissolved the nickel plate, leaving excessive voids and shrinkage cracks in the coating front-face surface. Several samples, brazed at 950° K with Sil-Bond #50 in flowing argon, were examined metallographically and showed good wettability and very little diffusion with minimum void areas. An explanation of the procedures used during the silver brazing attachment of coatings to the copper calorimeters is given as follows.

(1) The copper calorimeter surface to be coated was abraded lightly with 600-grit metallographic paper and cleaned with acetone to remove surface oxidation.

(2) The nickel-plated surface of the coating specimen was also cleaned with acetone.

(3) A 10-percent nitric acid solution was used to clean the silver-brazing alloy immediately before assembly.

(4) The sanded-copper surface, the nickel-plated surface, and the brazing alloy were coated with a watery thin coating of brazing flux to promote wettability.

(5) A graphite cylinder, 2.54 centimeters long and 0.73 centimeter inside diameter, was used as a brazing tool to ensure alinement and concentricity of the coating specimen and the copper calorimeter. The graphite cylinder was slipped over the calorimeter after the brazing alloy and coating specimen were assembled.

(6) The assembly to be brazed was placed in a nickel boat and inserted into a quartz tube furnace at 950° K for 5 minutes. An argon atmosphere flowing at 0.08 to 0.14 scm³/hr was used to ensure a nonoxidizing atmosphere during the brazing operation.

(7) After completion of the braze cycle, the brazed assembly was cooled for 15 minutes in the cooler portion of the tube furnace before removal.

(8) Rinsing in warm tap water permitted removal of the calorimeter from the graphite cylinder and removed the remaining traces of brazing flux. A final rinse with deionized water and a flush with methyl alcohol was performed, followed by drying with heated air.

b. A simulated calorimeter slug and a coating specimen that were prepared, assembled, and brazed at the same time as the copper calorimeters were mounted and polished for metallographic examination. Photomicrographs of the brazing trail samples and simulated calorimeter slug are shown in figures 3 to 5.

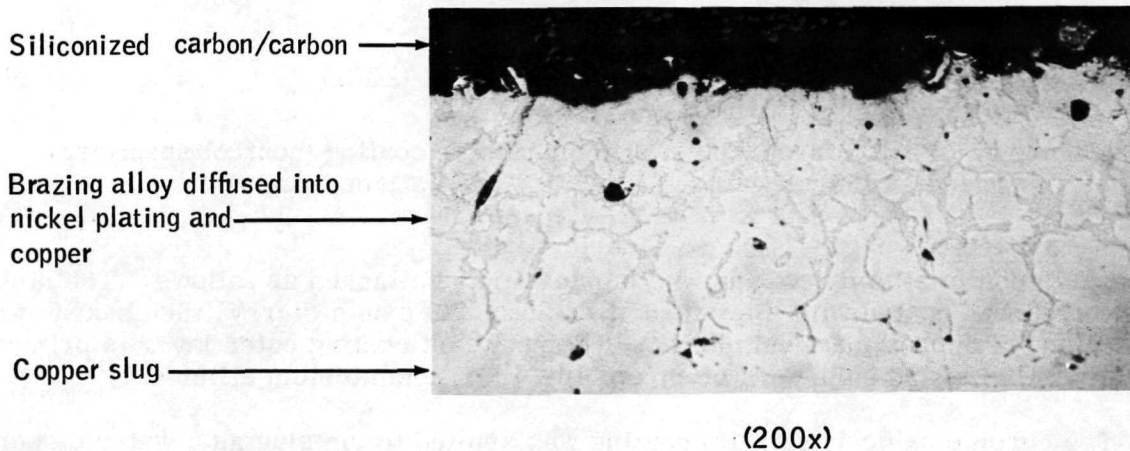


Figure 3. - Photomicrograph of silicon carbide coating (brazed trial specimen) brazed at 1172° K using QQ-S-561 Type 0 silver brazing alloy.

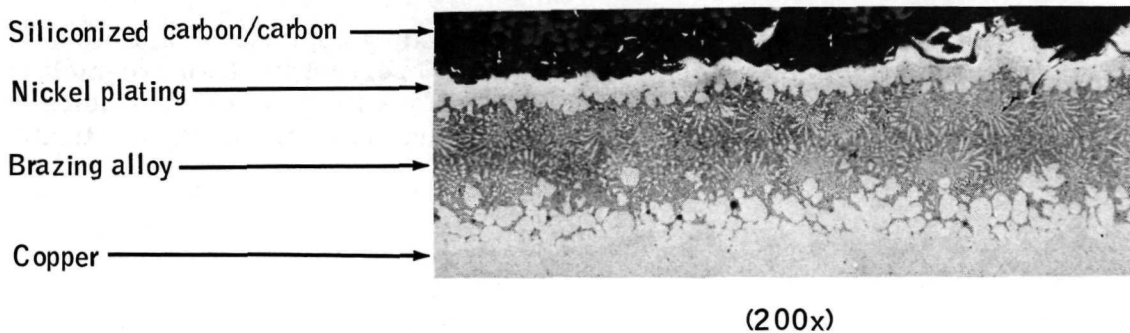


Figure 4. - Photomicrograph of silicon carbide coating (brazing trial specimen) brazed at 950° K using QQ-S-561 Type 4 silver brazing alloy.

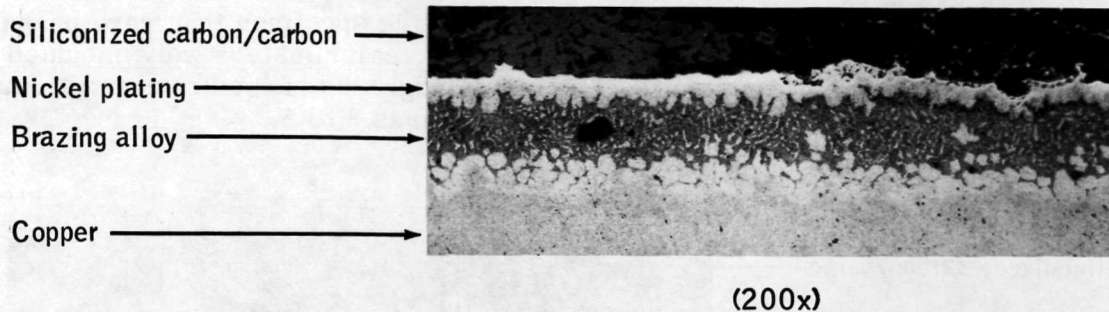


Figure 5. - Photomicrograph of silicon carbide coating (control specimen) brazed at 950° K using QQ-S-561 Type 4 silver brazing alloy.

The niobium silicide coating was fabricated and attached as follows. The niobium alloy Nb 752 was coated with a mixture of Si-20Cr-20Fe as a slurry, then baked at a temperature of approximately 1500° K. The resultant coating outer layer is primarily niobium disilicide and sublayers of chromium, iron, and niobium silicides.

The chrome oxide 1 (ref. 15) coating was applied to the slug as a water dispersion with a camel-hair brush. It was air dried overnight and fired at 811° K, instead of the standard 1200° K, for 30 minutes. The LI-0025 coating system consists of chromia dispersed in a borosilicate matrix and is 82.2 percent silica by weight. No glaze was applied because this process requires firing temperature in excess of 1200° K.

The chrome oxide 2 coating in borosilicate glass was flame sprayed onto the copper slugs on which a base enamel had been applied, then baked at 1100° K. The base enamel was 0.02 to 0.025 centimeter thick, and the chrome oxide coating was approximately 0.05 to 0.07 centimeter thick.

The silicon carbide/silicon coating was developed by application of a mixture of high-purity silicon carbide (80 percent) and silicon (20 percent) with an arc-melt spray on the oxidized-copper surface of the slugs. The surface reached a temperature of approximately 370° to 400° K. The temperature of the melt unit was approximately 2500° K.

REFERENCES

1. Fay, J. A.; and Riddell, R. R.: Theory of Stagnation Point Heat Transfer in Dissociated Air. *J. Aeron. Sci.*, vol. 25, no. 2, Feb. 1958, pp. 73-85.
2. Goulard, R.: On Catalytic Recombination Rates in Hypersonic Stagnation Heat Transfer. *Jet Propulsion*, vol. 28, 1958, pp. 737-745.
3. Chung, Paul M.: Hypersonic Viscous Shock Layer of Nonequilibrium Dissociating Gas. NASA TR R-109, 1961.
4. Inger, G. R.: Nonequilibrium Hypersonic Stagnation Flow with Arbitrary Surface Catalycity Including Low Reynolds Number Effects. *Int. J. Heat Mass Transfer*, vol. 9, 1966, pp. 755-772.
5. Tong, Henry; and Suzuki, Bob H.: Stagnation-Point Heat Transfer to Surfaces of Arbitrary Catalycity. *AIAA J.*, vol. 2, no. 11, 1964, pp. 2051-2052.
6. Chung, P. M.; Holt, J. F.; and Liu, S. W.: Merged Stagnation Shock Layer of Nonequilibrium Dissociating Gas, *AIAA J.*, vol. 6, no. 12, 1968, pp. 2372-2379.
7. Hartunian, R. A.; and Thompson, W. P.: Nonequilibrium Stagnation Point Heat Transfer Including Surface Catalysis. AIAA Paper No. 63-464, 1964.
8. Pope, Ronald B.: Stagnation-Point Convective Heat Transfer in Frozen Boundary Layers. AIAA Paper No. 68-15, 1968.
9. Hiester, Nevin K.; and Clark, Carroll F.: Feasibility of Standard Evaluation Procedures for Ablating Materials. NASA CR-379, 1966.
10. Lordi, J. A.; Mates, R. E.; and Moselle, J. R.: Computer Program for the Numerical Solution of Nonequilibrium Expansions of Reacting Gas Mixtures. NASA CR-472, 1966.
11. Gibson, W. E.; and Marrone, P. V.: A Similitude for Nonequilibrium Phenomena in Hypersonic Flight. *High Temperature Aspects of Hypersonic Flight*, Wilbur C. Nelson, ed., The MacMillan Co. (New York), 1964.
12. Gibson, W. E.; and Marrone, P. V.: Nonequilibrium Scaling Criterion for Inviscid Hypersonic Air Flows, CAL Report No. QM-1626-A-8, 1962.
13. Vinokur, M.: Hypersonic Flow Around Bodies of Revolution. Vol. I of General Research in Flight Sciences, part 1, Lockheed Missiles Report No. TR-288139, 1960.
14. Rosner, Daniel E.: Analysis of Air Arc-Tunnel Heat-Transfer Data. *AIAA J.*, vol. 2, 1964, pp. 945-948.
15. Anon.: Final Report for Development of a Rigidized Surface Insulation Thermal Protection System for Shuttle Orbiter. NASA CR-114958, 1971.



009 001 C1 U 33 730216 500120BS
PHILCO FORD CORP
AERONUTRONIC DIV
ATTN: TECH INFO SERVICES
FORD RD
NEWPORT BEACH CA 92663

POSTMASTER: If Undeliverable (Section 158
Postal Manual) Do Not Return

"The aeronautical and space activities of the United States shall be conducted so as to contribute . . . to the expansion of human knowledge of phenomena in the atmosphere and space. The Administration shall provide for the widest practicable and appropriate dissemination of information concerning its activities and the results thereof."

—NATIONAL AERONAUTICS AND SPACE ACT OF 1958

NASA SCIENTIFIC AND TECHNICAL PUBLICATIONS

TECHNICAL REPORTS: Scientific and technical information considered important, complete, and a lasting contribution to existing knowledge.

TECHNICAL NOTES: Information less broad in scope but nevertheless of importance as a contribution to existing knowledge.

TECHNICAL MEMORANDUMS: Information receiving limited distribution because of preliminary data, security classification, or other reasons. Also includes conference proceedings with either limited or unlimited distribution.

CONTRACTOR REPORTS: Scientific and technical information generated under a NASA contract or grant and considered an important contribution to existing knowledge.

TECHNICAL TRANSLATIONS: Information published in a foreign language considered to merit NASA distribution in English.

SPECIAL PUBLICATIONS: Information derived from or of value to NASA activities. Publications include final reports of major projects, monographs, data compilations, handbooks, sourcebooks, and special bibliographies.

TECHNOLOGY UTILIZATION PUBLICATIONS: Information on technology used by NASA that may be of particular interest in commercial and other non-aerospace applications. Publications include Tech Briefs, Technology Utilization Reports and Technology Surveys.

Details on the availability of these publications may be obtained from:

SCIENTIFIC AND TECHNICAL INFORMATION OFFICE

NATIONAL AERONAUTICS AND SPACE ADMINISTRATION

Washington, D.C. 20546